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MAGNETIC FIELD INDUCED CROSS RELAXATION BETWEEN TWO DIFFERENT S--ETC(U)

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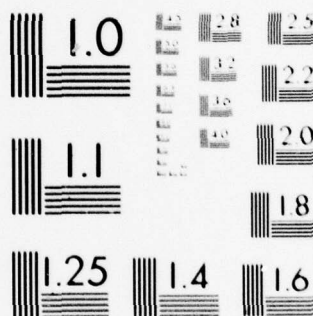
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MAGNETIC FIELD INDUCED CROSS RELAXATION  
BETWEEN TWO DIFFERENT SPIN TRANSITIONS  
OF TRIPLET COUMARIN

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Abstract

At certain magnetic fields, when the energy separations between the  $\tau_x - \tau_y$  spin levels and between the  $\tau_y - \tau_z$  levels of triplet coumarin become equal, intensity changes are observed in the phosphorescence of coumarin doped in a single crystal of durene cooled to 1.6°K that can be attributed to cross relaxation (CR) between the  $\tau_x - \tau_y$  spin levels of one triplet coumarin molecule and the  $\tau_y - \tau_z$  spin levels of another triplet coumarin. Rate equations that describe the time behavior of the populations of the spin levels which are involved in the CR process are described and numerically solved. CR behavior is found to be strongly dependent on the total coumarin triplet concentration.

## 1. Introduction

When two different spin systems present in a single crystal have equal or nearly equal Zeeman transition energies, but have different spin temperatures, magnetic energy transfer between the spin levels of the two systems can occur via cross relaxation (CR). This process has been extensively studied<sup>(1-2)</sup> in nuclear spin systems and has recently been observed in a number of electronic spin systems.<sup>(3-10)</sup>

Veeman and van der Waals<sup>(5)</sup> were the first to observe CR between phosphorescent triplet states and other spin systems isolated in a mixed molecular crystal at low temperatures. Since it changes the populations of the levels of spin-aligned systems, CR can be detected as changes in phosphorescence intensity. There have been a number of observations of the effects of CR on the phosphorescence intensity.<sup>(5-10)</sup>

Veeman et al.<sup>(5,6)</sup> have observed triplet-triplet CR between two like molecules, and triplet-radical CR in crystals of benzophenone and 4,4'-dibromobenzophenone (DBB) as well as between the electron spin transition of DBB and the bromine nuclear quadrupole transition. They have developed a thermodynamic description of the dynamics of this process for these systems.

Pitts and El-Sayed<sup>(9)</sup> found CR between the triplet state of tetrachlorobenzene (TCB) doped in a single crystal of durene and the doublet spin system of the photochemical product of durene host which is present in the crystal. They developed the kinetic rate equations that describe this process and were able to quantitatively predict the effect of CR on TCB phosphorescence intensity.

In this report we describe experimental studies of CR occurring between the spin levels of the triplet states of two coumarin molecules doped in a single crystal of durene. The kinetic rate expressions that describe this

process are developed. By numerically solving these equations we are able to fit the dynamical behavior of the coumarin spin level populations upon applying a magnetic field of magnitude and direction necessary to induce CR and to predict the dependence of this CR effect on the concentrations of the coumarin triplets.

## 2. Description of the System

The zero field dynamic properties of the  $T_1$  state of coumarin doped in a single crystal of durene have been measured by Hirota and his coworkers.<sup>(11,12)</sup> We have remeasured these parameters and find our results to be in very good agreement with their values. High field single crystal EPR studies<sup>(13)</sup> indicate that coumarin fits substitutionally into the durene crystal with the molecular axes (M, L, N) of both molecules coincidental (see Fig. 1). The z magnetic spin axis, and the x and y spin axes, of triplet coumarin are parallel and perpendicular to the carbonyl bond respectively, and the y and z axes are in the plane of the molecule. Coumarin substitutes in durene in two orientations, related by rotation about the L molecular axis. When a magnetic field is aligned along the  $c'$  axis of the durene crystal (which is about  $6^\circ$  off the M molecular axes for both orientations), the field is aligned about  $30^\circ$  away from the z-axis of all coumarin molecules.

The populating and the depopulating routes of the  $T_1$  state of coumarin in zero field are shown in Fig. 1. The low field Zeeman effects on the 0,0 band and the  $0,830\text{ cm}^{-1}$  vibronic band phosphorescence intensities have been studied, and the results agree with the indirect mechanism shown.<sup>(14)</sup> The experimentally observed steady state values of the intensity of the 0,0 band phosphorescence in the applied magnetic field relative to the 0,0 band intensity in zero field ( $I^H(0,0)/I^0(0,0)$ ) are shown in Fig. 2a for the field directed along the durene  $c'$  axis. The abrupt decrease in intensity around

465 G cannot be attributed to changes in the triplet state populations induced solely by the applied field. In order to determine whether CR was a possible cause of the intensity decrease, calculations were made to determine the energy separations for all the spin systems expected to be present in a single crystal of durene doped with coumarin as a function of magnetic field strength. These calculations show no equalization of the energy separations of the triplet spin systems of coumarin with that of the triplet systems of duraldehyde, an impurity present in durene, in the region of 300-600 G. Furthermore, the energy splittings between the spin levels of the coumarin triplet do not equal that of a doublet spin system ( $\Delta E = g\beta H$  where  $g$  is the  $g$  value for a free electron,  $\beta$  is the Bohr magneton and  $H$  is the applied magnetic field strength) at fields less than 1 kg. This rules out CR between the spin systems of coumarin triplet molecules and the spin systems of duraldehyde triplet molecules or any radical photoproducts. However, calculations do show that at 465 G the  $\tau_x - \tau_y$  and the  $\tau_y - \tau_z$  energy splittings for the coumarin triplet itself become equal. Intermolecular CR between the  $\tau_x - \tau_y$  of one coumarin triplet and the  $\tau_y - \tau_z$  spin transitions of another offers a possible explanation for the observed intensity change.

The 0,0 band of the coumarin phosphorescence is known to originate<sup>(11,12)</sup> primarily from the  $\tau_y$  level (see Fig. 1). At low magnetic fields, the  $\tau_y$  level is the most populated. The double spin flip between the  $\tau_x$  and the  $\tau_y$  levels and between the  $\tau_y$  and  $\tau_z$  levels occurring during CR will result in a net decrease of population in the  $\tau_y$  level and hence a decrease in the 0,0 band phosphorescence intensity. In agreement with this explanation the phosphorescence of the  $0.830 \text{ cm}^{-1}$  vibronic band of coumarin, which arises mainly from the  $\tau_z$  level, is found to increase in intensity at magnetic fields where CR takes place.

The PMDR signals for the  $\tau_x - \tau_y$  and for the  $\tau_y - \tau_z$  transitions of coumarin at the magnetic field strengths in the region of CR show overlap of these two transitions to occur in the region where the phosphorescence intensity of the 0,0 band decreases. (see Fig. 2). Thus, at the magnetic field strengths where the frequencies of the two transitions are made equal to within the width of the states, the two spin systems come into new steady state via a double spin flip process.

### 3. Experimental Methods

The single crystals used in this study were grown by the Bridgman method using zone refined durene doped with vacuum sublimed coumarin. The crystals were aligned conoscopically in such a manner that the magnetic field was directed along the  $c'$  crystal axis. Magnetic fields were generated by a superconducting magnet. The magnet, spectrometer and electronic detection systems have all been described previously.<sup>(15)</sup> The magnetic field change of 0  $\rightarrow$  465 G was induced by electronically controlling the current supplied to the magnet. The time required for the magnet to reach a steady state following a change in current was less than 30 ms. The time behavior of the phosphorescence was accumulated in the memory of a Northern NS-570A CAT (computer averaged transients) which was triggered just prior to the change of the field. All experiments were conducted in a liquid helium cryostat pumped to 1.6 K. The 3130 Å line of a 100 W high pressure mercury lamp was used as the primary source of excitation. The intensity of the output of this lamp was changed by the use of neutral density filters. The coumarin phosphorescence intensity was found to vary linearly with exciting light intensity demonstrating that the total coumarin triplet concentration was directly proportional to the exciting light intensity.

### 4. Experimental Results

The effect of CR was studied by observing the behavior of coumarin phosphorescence intensity when the external magnetic field was changed from a

value which does not induce CR (0 Gauss, in this case) to  $465 \pm 5$  G (the maximum of CR). In general, following the change in the field, a time behavior was observed before a new steady state was reached. This time behavior was found to be strongly dependent on the concentration of coumarin doped in the durene as well as the intensity of the light used to excite the coumarin. This implies that the rate of CR is dependent on the concentration of coumarin triplets present in the crystal.

As shown in Fig. 3, at high coumarin doping concentrations ( $> 0.5$  molar percent) and/or high exciting light intensities the time behavior manifests itself as a very fast decrease in 0,0 band phosphorescence intensity followed by a slower slight increase to the new steady state intensity that is lower than expected in the absence of CR. Further increases in either the coumarin concentration or the exciting light intensity do not change either the time behavior or the steady state value of  $I^H(0,0)/I^0(0,0)$  (see Figs. 3 and 4).

At low coumarin concentrations and low light intensities the time behavior exhibits a relatively slow increase in phosphorescence intensity to a steady state  $I^H(0,0)/I^0(0,0)$  value of  $\approx 1.20 \pm .02$  (see Fig. 4). This is the value of  $I^H(0,0)/I^0(0,0)$  expected in the absence of CR, obtained by extrapolating the low field Zeeman phosphorescence curve in Fig. 2 to the field where CR takes place. Lowering further either the coumarin concentration or the exciting light intensity does not change the time behavior or the steady state phosphorescence intensity. Thus, in the limit of very low coumarin triplet concentrations, it appears as if no CR occurs.

Intermediate values of coumarin doping concentrations and/or intensities of the exciting light give steady state  $I^H(0,0)/I^0(0,0)$  values and dynamic behaviors of 0,0 band intensity between these two extremes. In these regions, the CR process occurs on the same time scale as the population changes of the coumarin triplet levels induced by the magnetic field.

That the CR effect depends only on the total coumarin triplet concentration is clear from the fact that we were able to obtain reproducible results from crystals with different doping concentrations of coumarin. It was possible to correlate the exciting light intensity dependences on the CR effect on phosphorescence intensity for the different crystals. This was done by setting the steady state  $I^H(0,0)/I^0(0,0)$  value of  $0.99 \pm .02$ , obtained in different sets of experiments, to correspond to an arbitrary value of the exciting light intensity ( $I = 0.52$ ) and normalizing the other intensities accordingly. When this was done excellent agreement was obtained for the intensity dependence of CR for differently doped crystals, even though the maximum intensity of the exciting light may vary for each experiment.

##### 5. Theoretical Model for the CR Dynamics

The rate equations for the three triplet levels in a magnetic field,  $H$ , in the absence of CR, are <sup>(15)</sup>

$$dN_i/dt = K_i^H - k_i^H N_i \quad (i = x, y, z) \quad (1)$$

where  $N_i$  is the population in the triplet spin level  $i$  and  $K_i^H$  and  $k_i^H$  are the populating rate and total decay rate constant of level  $i$ . These equations assume isolated phosphorescent guest molecules in a host single crystal with well-defined orientations and known static and dynamic properties. Spin lattice relaxation (SLR) rates are assumed slower than the  $k_i^H$  so that the spin level populations are aligned.

When a magnetic field is applied such that the energy separation between the  $\tau_x$  and  $\tau_y$  levels equals that between the  $\tau_y$  and  $\tau_z$  levels, CR is possible between these two sets of spin levels on two different molecules. Such a CR event

can result in one of two possible changes in the spin level populations. A spin from the  $\tau_y$  level of one coumarin molecule can flip down to the  $\tau_x$  level while simultaneously a spin from the  $\tau_y$  level of the second molecule flips up to the  $\tau_z$  level. The reverse process, where the spins in the  $\tau_x$  and  $\tau_z$  levels are transferred to the  $\tau_y$  levels of the two molecules, occurs with equal probability. Thus each CR event leads to a net change of two in the  $\tau_y$  spin level population and a net change of one in the  $\tau_x$  and  $\tau_z$  spin levels. This is the source of the factor of 2 in the rate equations below.

It has been shown<sup>(3,9)</sup> that the probability that an upper spin in one system flips down in energy simultaneously as a lower spin in the second system flips up is given by the CR probability times the product of the spin populations in the upper level of the first system and the lower level of the second. Using this relation, the rate equations for the triplet spin levels in the presence of CR become

$$\begin{aligned} dN_x/dt &= K_x^H - k_x^H N_x - k_{CR} N_x N_z + k_{CR} N_y N_y \\ dN_y/dt &= K_y^H - k_y^H N_y - 2k_{CR} N_y N_y + 2k_{CR} N_x N_z \\ dN_z/dt &= K_z^H - k_z^H N_z - k_{CR} N_x N_z + k_{CR} N_y N_y \end{aligned} \quad (2)$$

where  $k_{CR}$  is the effective CR rate constant. SLR between the triplet spin levels are neglected since these experiments were performed at 1.6°K.

The effect of changes in the triplet spin populations on the phosphorescence intensity of a particular vibronic band is described by the following equation:

$$I^H(\nu) = \sum_{i=1}^3 (r_k^H)_i N_i \quad (3)$$

where  $r_{k_i}^H$  are the radiative rate constants in field  $H$  for the spin level  $i$  to vibronic band  $v$ . In the absence of CR, the  $N_i$  are found by solving equation (1); if CR is occurring, the  $N_i$  are obtained from equation (2). In general, the populations will not be in steady state and the phosphorescence intensity will be a function of time.

## 6. Calculations

The experimental results for the dynamic behavior of CR, shown in Fig. 3, give a good indication of the effect of  $k_{CR}$  on  $I^H(0,0)/I^0(0,0)$  and its dependence on coumarin triplet concentrations. If they are correct, the rate expressions described above should predict the experimentally observed time behavior and triplet concentration dependence.

A Fortran program for use with an IBM 360 Model 91 computer was written to calculate  $I^H(0,0)/I^0(0,0)$  (using equation (3)) as a function of time. The time dependences of  $N_i$  were obtained by numerically solving the coupled differential equations in (2). The input parameters required for the program are the spin populations of the three triplet levels at time = 0, the relative populating and radiative decay rate constants, the total decay rate constants for each level, an estimate of  $k_{CR}$  and the relative intensity of the exciting light. The values of these parameters are given in Table 1.

It has been shown<sup>(16)</sup> that the total decay rates and relative radiative decay rates for a phosphorescing molecule in a single crystal with known dynamic and static zero field properties and orientation can be calculated exactly for a given magnetic field value along a specific direction. These values have been calculated for coumarin in durene for a field of 465 G along the durene  $c'$  axis. The ISC mechanism for coumarin is clearly indirect, but we have not as yet been able to calculate the relative populating rates for the three

spin levels at 465 G exactly, due to insufficient knowledge about the upper triplet(s) involved in the ISC process. Instead, we have estimated a set of rates based on low field Zeeman phosphorescence results extrapolated to zero CR at 465 G and on PMDR results at 465 G. The triplet concentrations in zero field were set to an estimated value of  $10^{15}$  spins/cm<sup>3</sup>, and the populating rates were normalized accordingly. The value for  $k_{CR}$  ( $0.35 \times 10^{-14}$  spins<sup>-1</sup> sec<sup>-1</sup>) was chosen so that the best agreement with experimental results at an intermediate intensity (steady state  $I^H(0,0)/I^O(0,0) = 0.99$ ) was obtained.

Fig. 3 shows the experimental and the calculated time behavior of  $I^H(0,0)/I^O(0,0)$  following the application of a field change of 0 → 465 G.  $k_{CR}$  was initially assumed to be independent of exciting light intensity and triplet concentration (see Fig. 3i). In this case the calculated time behavior agrees fairly well qualitatively with the experimental results. However, the calculations do not show the strong dependence on exciting light intensity observed experimentally.

$k_{CR}$  was then made proportional to the square root of the triplet concentration (and thus proportional to the square root of the intensity of the exciting light). Fig. 3ii shows very good agreement between calculated and experimentally observed changes in the time behavior and magnitude of  $I^H(0,0)/I^O(0,0)$ . Calculations show the observed dependence of the steady state  $I^H(0,0)/I^O(0,0)$  values on triplet concentration and on exciting light intensity.

Next  $k_{CR}$  was chosen to be proportional to the intensity of the exciting light (and, hence, proportional to the triplet concentration). As seen in Fig. 3iii, there is also very good agreement between predicted and observed behavior with respect to both steady state  $I^H(0,0)/I^O(0,0)$  values and transient curves. The calculations show the observed exciting light intensity dependence. Calculated changes in time behavior and magnitude of  $I^H(0,0)/I^O(0,0)$  as the concentration

of triplets is changed are also in good agreement with experiment.

Fig.3iv shows the predicted time behavior of  $I^H(0,0)/I^0(0,0)$  when  $k_{CR}$  was made proportional to the square of the triplet concentration (i.e., proportional to the square of the intensity of exciting light). Again there is fairly good agreement between predicted and observed results for the qualitative time behavior of  $I^H(0,0)/I^0(0,0)$ . However, the magnitudes of the  $I^H(0,0)/I^0(0,0)$  values predicted when  $k_{CR} \propto T_{exc}^2$  indicate a stronger triplet concentration dependence than is observed experimentally.

It appears that the kinetic rate expressions discussed above provide a reasonable model to describe the dynamic behavior of CR between the  $\tau_x - \tau_y$  and the  $\tau_y - \tau_z$  spin level systems of coumarin in durene when the effective CR rate constant is proportional either to the square root of the coumarin triplet concentration or to the concentration of coumarin triplets present in the crystal. Experimental accuracy is not sufficient to distinguish between  $k_{CR} \propto T^{0.5}$  and  $k_{CR} \propto T^{1.0}$ .

## 7. Discussion

The time behavior of the phosphorescence intensity at 465 G (Fig. 3) is due to the competition among the populating, depopulating and CR rate processes described by equation (2) and shows the recovery of the spin levels of coumarin initially at their steady state zero field populations to their final steady state populations at 465 G. These populations are determined both by the populating and decay rates in the magnetic field and by the rate of the CR processes.

At high triplet concentrations the CR process dominates. This is apparent by the very rapid decrease in phosphorescence  $I^H(0,0)/I^0(0,0)$  value upon application of the magnetic field followed by the slower return to the steady state value. This value of  $I^H(0,0)/I^0(0,0)$  is still much less than that expected in the absence of CR. The net effect of CR is to transfer population from the radiative  $\tau_y$  level to the  $\tau_x$  and  $\tau_z$  levels. Thus the extent of CR is manifested not only by the time behavior of phosphorescence intensity immediately after application of the field but also by the observation that the steady state  $I^H(0,0)/I^0(0,0)$  value with CR is much less than the steady state value expected without CR.

As the concentration of coumarin triplets decreases, the rate of CR is decreased. This is apparent in the time behavior curves which show both the gradual loss of the initial fast decrease in  $I^H(0,0)/I^0(0,0)$  due to CR upon application of the field and the gradual increase in the steady state  $I^H(0,0)/I^0(0,0)$  value expected in the total absence of CR.

As has already been shown, good agreement between experimental and calculated behavior is obtained when it is assumed that the value of  $k_{CR}$  is proportional either to the triplet concentration or to the square root of the triplet concentration. This implies that for a given total concentration of triplets (in zero field) second order rate kinetics describe the CR process but that the rate constant for CR is itself dependent on the total concentration of triplets present in the crystal. Our results appear to be in agreement with Lin et al.<sup>(4)</sup> who found that the probability of CR between trapped electrons and radicals in organic glasses went as  $f^{0.4} - f^{0.6}$ , where  $f$  is the fraction of molecular sites in the glass occupied by radicals.

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## References

1. N. Bloembergen, S. Shapiro, P. S. Pershan, and J. O. Artman, *Phys. Rev.*, 114, 445 (1959).
2. W. B. Mims and J. D. McGee, *Phys. Rev.*, 1233 (1960).
3. H. Yoshida, D. Feng, and L. Kevan, *J. Chem. Phys.*, 58, 4924 (1973).
4. D. P. Lin, D. F. Feng, F. Q. H. Ngo and L. Kevan, *J. Chem. Phys.*, 65, 3994 (1976).
5. W. S. Veeman and J. H. Van der Waals, *Chem. Phys. Lett.*, 7, 65 (1970).
6. W. S. Veeman, A. L. J. Van der Poel and J. H. Van der Waals, *Mol. Phys.*, 29, 225 (1975).
7. J. H. Lichtenbelt, J. G. F. M. Fremeijer, H. Veenvliet, and D. A. Wiersma, *Chem. Phys.*, 10, 107 (1975).
8. J. H. Lichtenbelt, J. G. F. M. Fremeijer and D. A. Wiersma, *Chem. Phys.*, 18, 93 (1976).
9. W. M. Pitts and M. A. El-Sayed, *Chem. Phys.*, 25, 315 (1977).
10. J. A. Mucha and D. W. Pratt, *J. Chem. Phys.*, 66, 5356 (1977).
11. E. T. Harrigan and N. Hirota, *Chem. Phys. Lett.*, 27, 405 (1974).
12. E. T. Harrigan and N. Hirota, *Mol. Phys.*, 31, 663 (1976).
13. E. T. Harrigan, A. Chakrabarti and N. Hirota, *J. Am. Chem. Soc.*, 98, 3460 (1976).
14. C. Gniazdowski and M. A. El-Sayed, unpublished results.
15. W. M. Pitts and M. A. El-Sayed, *Chem. Phys.*, 19, 289 (1977).
16. M. A. El-Sayed and R. W. Leyerle, *J. Chem. Phys.*, 62, 1579 (1975).
17. C. Kittel and E. Abrahams, *Phys. Rev.*, 90, 238 (1953).

**TABLE 1: Input Parameters Used to Calculate CR Effects on the 0-0 Band  
Phosphorescence Intensity of Coumarin at a Field of 450 G Along the Durene  
c' Axis.**

	$\tau_x$	$\tau_y$	$\tau_z$
ZF Populations ( $\frac{\text{spins}}{\text{cc}}$ )	$0.39 \times 10^{15}$	$0.36 \times 10^{15}$	$0.25 \times 10^{15}$
ZF ISC Rates ( $\frac{\text{spins}}{\text{sec}}$ )	$0.12 \times 10^{15}$	$0.72 \times 10^{15}$	$2.43 \times 10^{15}$
ZF Decay Rates ( $\text{s}^{-1}$ )	0.32	2.00	9.70
ZF Rel. Rad. Decay	0.10	4.00	1.00
450 G ISC Rates ( $\frac{\text{spins}}{\text{sec}}$ )	$0.34 \times 10^{15}$	$0.91 \times 10^{15}$	$1.36 \times 10^{15}$
450 G Decay Rates ( $\text{s}^{-1}$ )	0.92	1.88	9.22
450 G Rel. Rad. Decay	0.45	3.64	1.01

* $k_{\text{CR}}$ independent of T	$0.35 \times 10^{-14}$	$\text{spins}^{-1}$	$\text{s}^{-1}$
* $k_{\text{CR}} \propto T^{0.5}$	$0.49 \times 10^{-14}$	$\text{spins}^{-1}$	$\text{s}^{-1}$
* $k_{\text{CR}} \propto T^{1.0}$	$0.68 \times 10^{-14}$	$\text{spins}^{-1}$	$\text{s}^{-1}$
* $k_{\text{CR}} \propto T^{2.0}$	$1.29 \times 10^{-14}$	$\text{spins}^{-1}$	$\text{s}^{-1}$

\* These values of the CR probability correspond to a total coumarin triplet concentration of  $1.0 \times 10^{15}$  spins/cc.

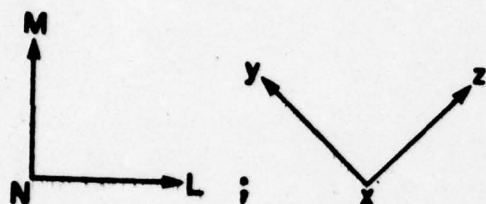
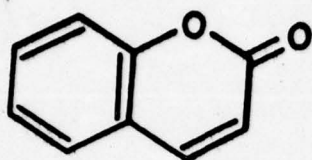
### Figure Captions

- Fig. 1 The molecular axis system (M,L,N) of coumarin and durene. In the crystal, coumarin replaces durene with the molecular axis system coincidental. The spin axes (x,y,z) of coumarin are parallel to (z) and perpendicular to (x,y) the carbonyl bond.<sup>(13)</sup> The bottom portion of the figure shows the decay route and a probable populating scheme for the  $T_1$  state of coumarin in zero field.
- Fig. 2a Experimentally observed steady state values of  $I^H(0,0)/I^0(0,0)$  for coumarin doped in a durene crystal as a function of magnetic field strength along the durene c' axis. The dots represent averages of at least six measurements and the vertical bars represent standard deviation. The dashed curves show the calculated  $\tau_x - \tau_y$  and the  $\tau_y - \tau_z$  transition frequencies (right ordinate) as a function of the field.
- Fig. 2b Experimentally observed PMDR signals for the  $\tau_x - \tau_y$  and  $\tau_y - \tau_z$  transitions as a function of microwave frequency at various fields applied along the durene c' axis.

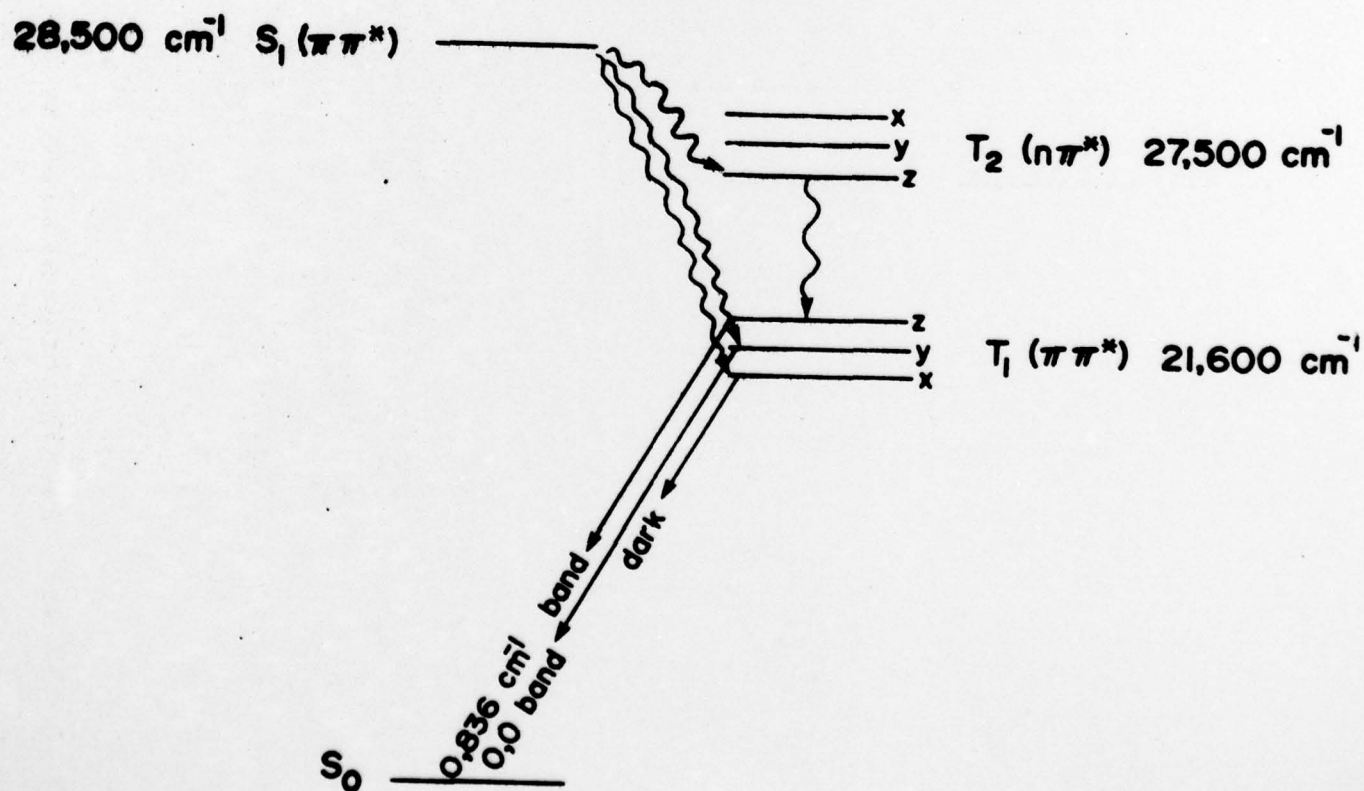
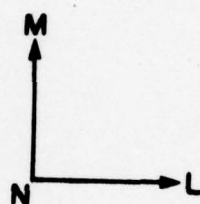
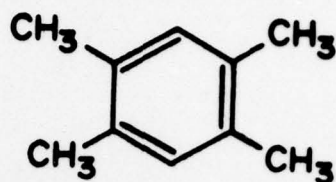
Fig. 3 A comparison of the calculated (broken curves) and the observed (solid curves) time behavior of the coumarin phosphorescence intensity following the application of a magnetic field inducing CR at time = 0. Curves a, b, c, and d show the experimentally observed behavior for the relative intensities of exciting light 0.80, 0.42, 0.16 and 0.08, respectively. (These intensities are relative to the total unfiltered lamp intensity.) Curves a', b', c', and d' show the corresponding calculated time behavior at these intensities. i shows the calculations for  $k_{CR}$  independent of the total coumarin triplet concentrations, T; ii the calculations for  $k_{CR} \propto T^{0.5}$ ; iii the calculations for  $k_{CR} \propto T^{1.0}$  and iv the calculations for  $k_{CR} \propto T^{2.0}$ . The values of the input parameters used in these calculations are given in Table 1, except that in each calculation the values of the ISC rates and the ZF populations at  $t = 0$  have been multiplied by the relative intensity of the exciting light. The values of  $k_{CR}$  have been adjusted accordingly for each intensity.

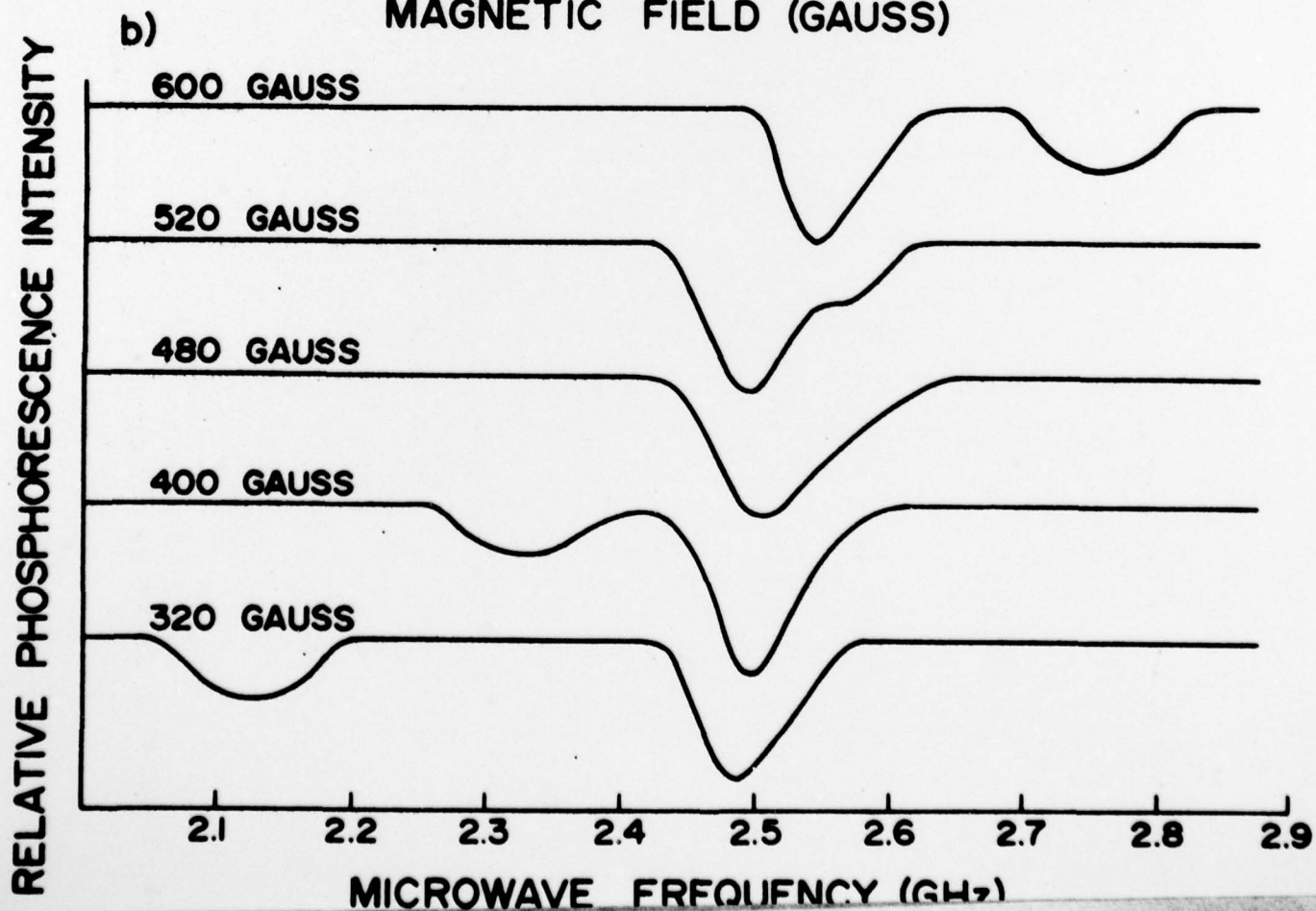
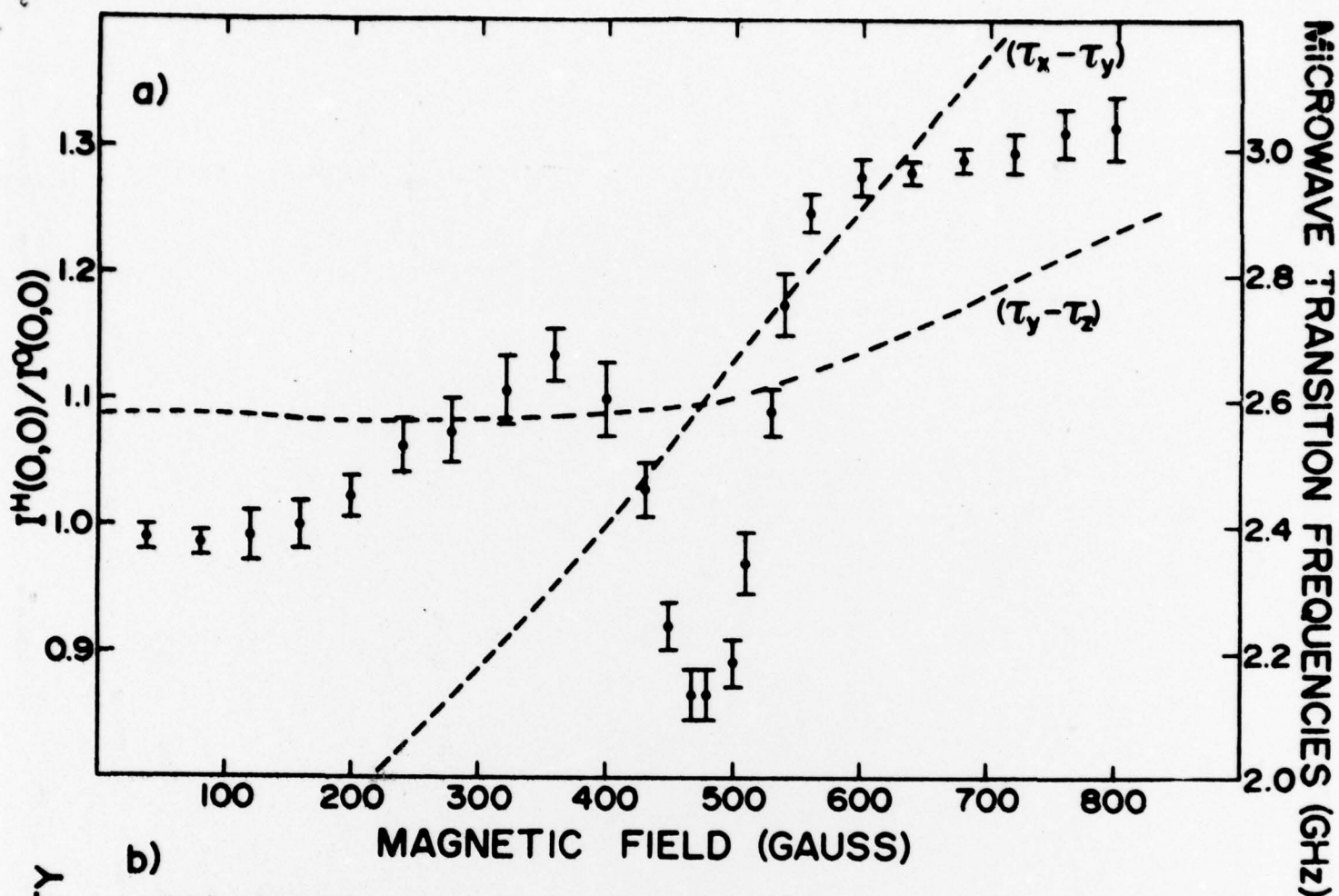
Fig. 4 The normalized phosphorescence intensity of the 0,0 band of coumarin in durene at 465 G along the durene c' crystal axis as a function of the relative intensity of the exciting light. Each point represents the average of at least two measurements. Error bars reflect average deviations of these measurements. The curves are the calculated magnitudes of  $I^H(0,0)/I^0(0,0)$  assuming a)  $k_{CR} \propto T^{0.0}$ , b)  $k_{CR} \propto T^{0.5}$ , c)  $k_{CR} \propto T^{1.0}$  and d)  $k_{CR} \propto T^{2.0}$  where T is the total coumarin triplet concentration and is proportional to the exciting light intensity.

COUMARIN

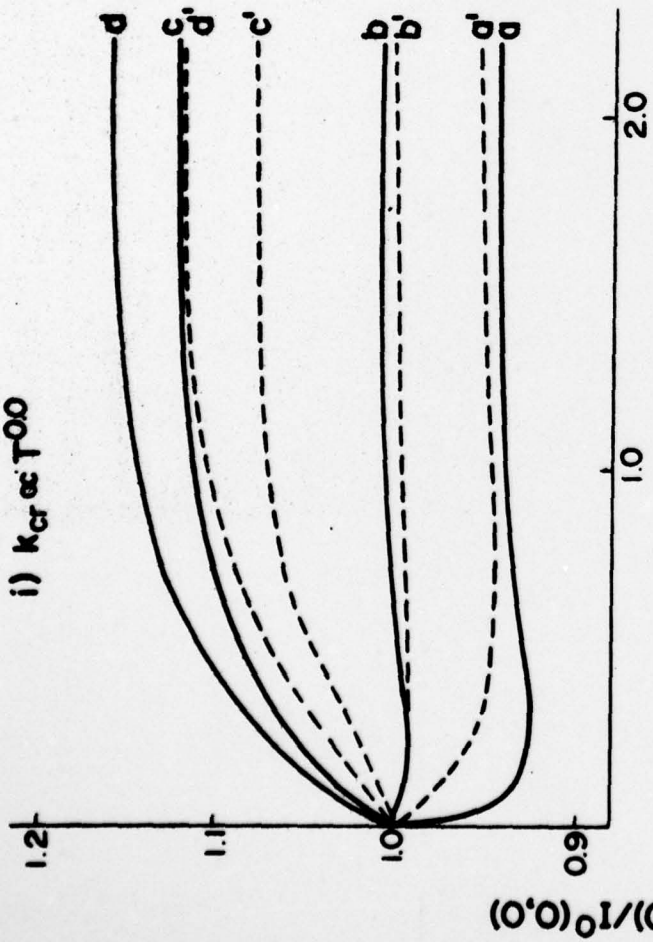


DURENE

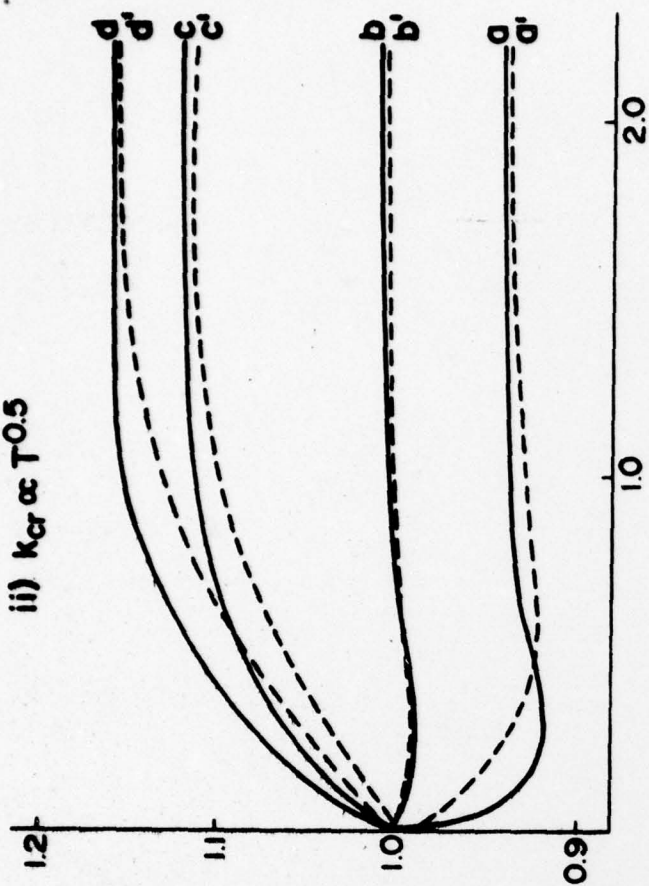




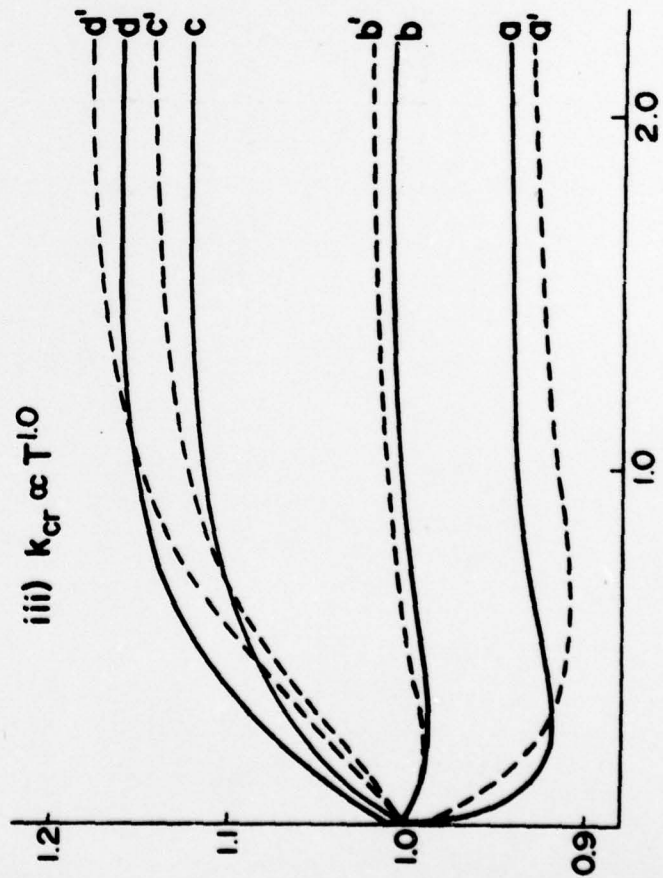
i)  $k_{cr} \propto T^{0.0}$



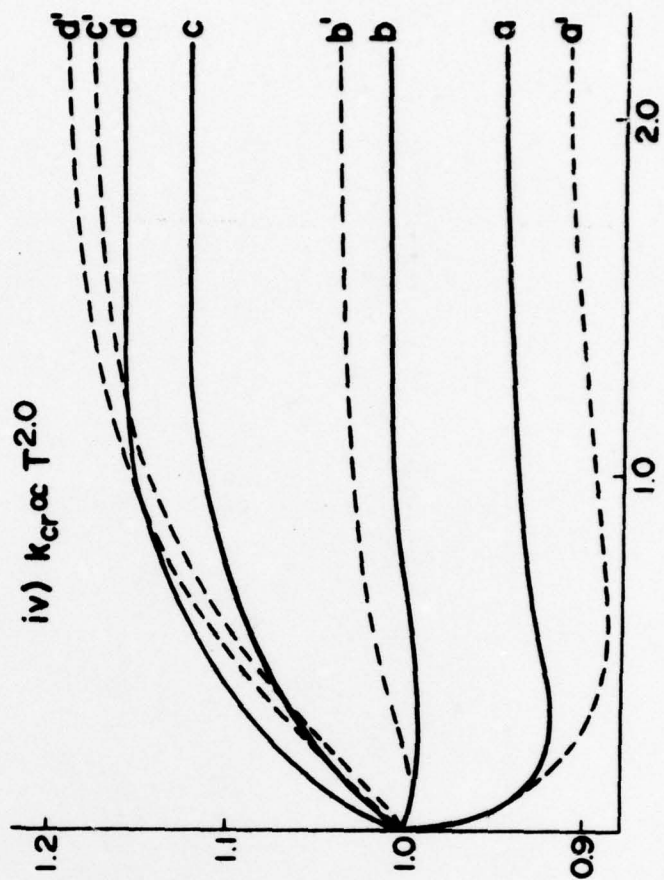
ii)  $k_{cr} \propto T^{0.5}$



iii)  $k_{cr} \propto T^{1.0}$

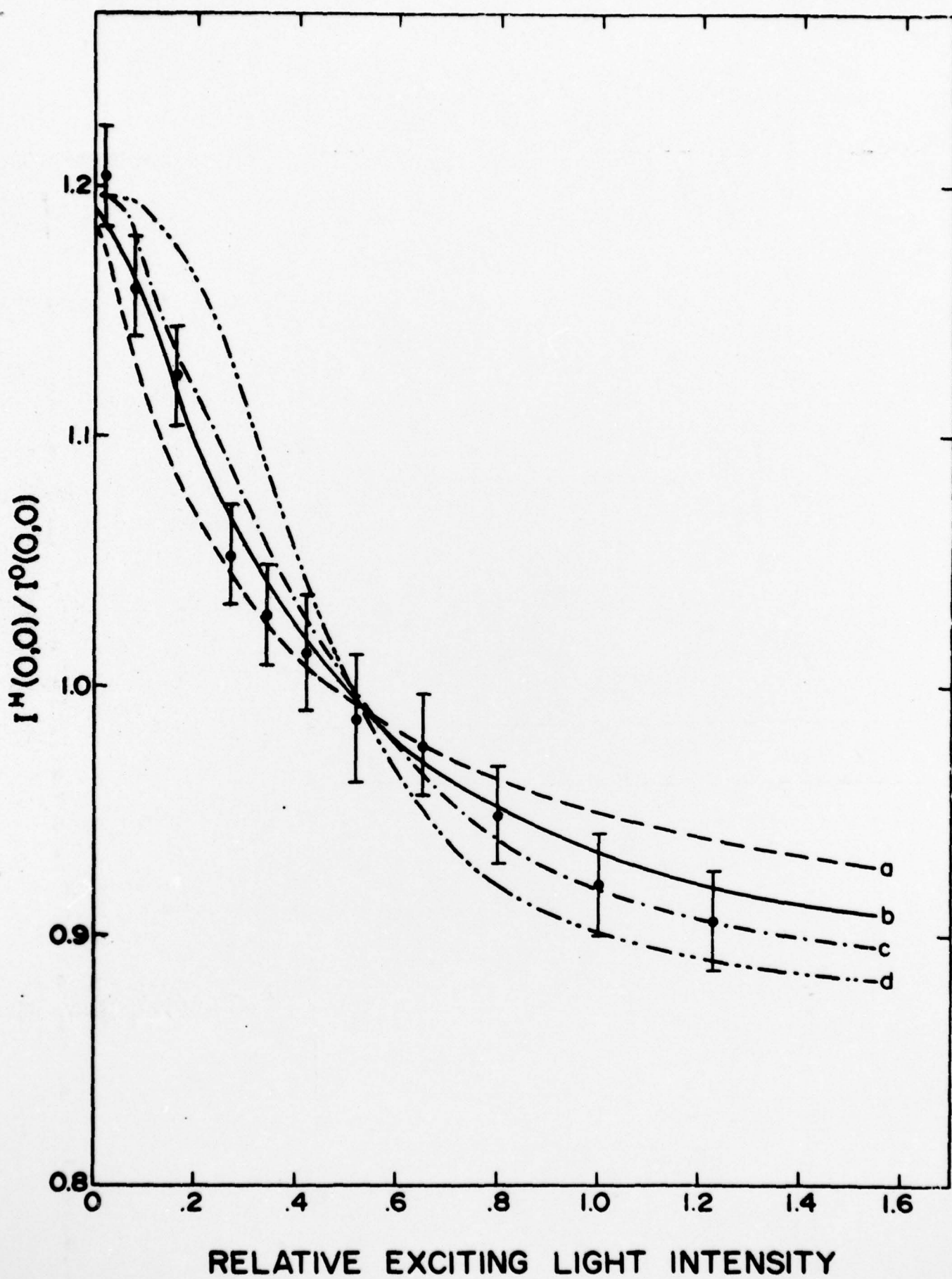


iv)  $k_{cr} \propto T^{2.0}$



TIME (s)

$I(0,0)/I(0,0)_H$



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